

# Probing the local chemical bonding of interfacial S atoms in CdS/ZnSe superlattices

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## INTRODUCTION

To investigate the chemical environment of buried atoms is an experimental challenge, requiring a spectroscopic technique which is atom-specific, chemically sensitive, non-destructive, and furthermore able to probe atoms buried within a film or solid sample. These experimental requirements can be met by X-ray emission spectroscopy (XES) at a high-flux (undulator) synchrotron beamline such as beamline 8.0. In the present study, we have investigated superlattices of CdS and ZnSe and utilized an interesting feature in S  $L_\alpha$  XES spectra, namely a cross-transition from metal d-states into S 2p core holes ionized by the synchrotron radiation. As will be shown, we can utilize a small (approx. 0.5 eV) binding energy difference between Zn 3d and Cd 4d states to unambiguously determine the chemical environment of the probed S atoms, i.e., whether the S atoms are predominantly bound to Cd or Zn neighbors. This approach can then be utilized to investigate the intermixing at buried interfaces in CdS/ZnSe superlattices.

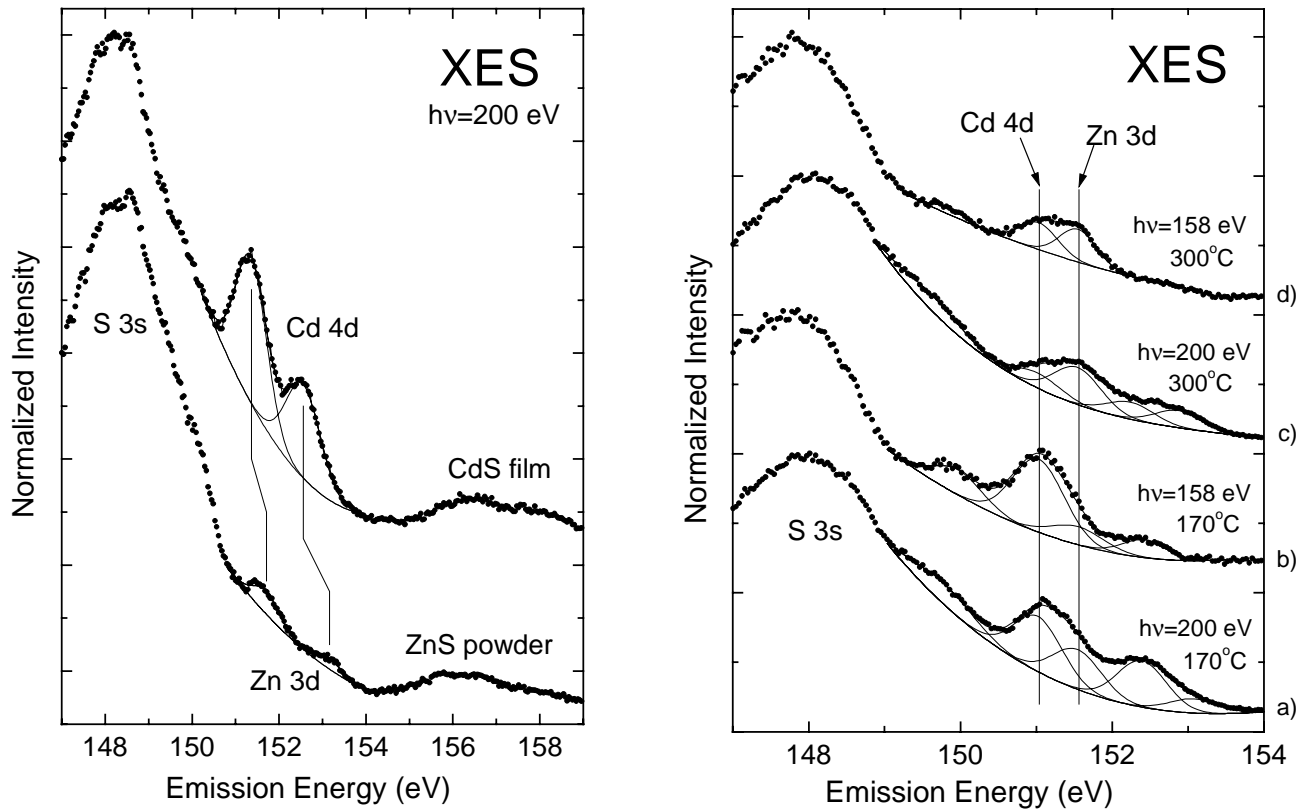
## EXPERIMENTAL

CdS/ZnSe short-period superlattices were prepared by conventional molecular beam epitaxy [1]. They consist of 200 symmetric periods of ZnSe and cubic CdS with a period length of about 3 nm on top of a ZnSe buffer layer. Two different samples were investigated, differing by the chosen growth temperatures of  $\approx 170^\circ\text{C}$  and  $\approx 300^\circ\text{C}$ , respectively. Due to the different growth temperatures, different degrees of intermixing at the buried superlattice interfaces can be expected.

The experiments were performed by employing the soft X-ray fluorescence (SXF) spectrometer at beamline 8.0. To achieve maximum energy resolution for the detected photons, an entrance slit of 50  $\mu\text{m}$  was utilized in the SXF spectrometer, while the monochromator of beamline 8.0 was operated in a high-flux, low-resolution mode.

## RESULTS

The investigation and analysis of high-resolution S  $L_\alpha$  XES spectra of various sulfides (including ZnS and CdS) dates back to (at least) 1968 [2]. The high flux offered by third generation synchrotrons and the advantage of excitation energy tunability has since then allowed a detailed understanding of the various contributions to the ZnS and CdS S  $L_\alpha$  XES spectra [3]. In the present context, the identification of Cd  $\rightarrow$  S and Zn  $\rightarrow$  S cross transitions is of particular importance. As shown in Fig. 1, a high-resolution investigation of ZnS and CdS reference samples reveals X-ray emission from metal d states (3d in the case of Zn and 4d in the case of Cd) into the S  $2p_{1/2}$  and  $2p_{3/2}$  core levels, at emission energies of about 151.0-151.5 eV and about 152.5-153.0 eV, respectively. As depicted in Fig. 1, a shift of the metal d states is observed between ZnS and CdS, which stems from the binding energy difference of Zn 3d and Cd 4d states in these compounds (about 0.5 eV).



Note that the intensity of the Zn 3d peaks is substantially lower than that of the Cd 4d peaks (normalized with respect to the S 3s peak intensity at 148.2 eV). While this result may be obscured by the sample quality of the ZnS powder, it is in accord with the results obtained in various other publications (e.g. [2] and [3]). This suggests that the wavefunction overlap of the Zn 3d states with the S 2p states is smaller than in the Cd case, as can be expected from the spatial expansion of 3d and 4d wavefunctions, respectively.

Figure 2 presents the corresponding S  $L_{\alpha}$  X-ray emission spectra for two different ZnSe/CdS superlattices, grown at 170 °C (a, b) and at 300 °C (c, d), respectively. The spectra were taken at excitation energies of  $h\nu=200$  eV (a, c) and  $h\nu=158$  eV (b, d) in order to separate the contributions from S  $2p_{1/2}$  and S  $2p_{3/2}$  core holes. At  $h\nu=158$  eV, the amount of S  $2p_{1/2}$  core holes is strongly reduced, and hence the metal d-state features at emission energies above 152 eV are strongly diminished (spectra b and d).

By visual inspection of the raw data it becomes evident that the energy region between 150.5 and 152.0 eV, i.e., the region where the metal d-state transition into the S  $2p_{3/2}$  core hole is observed, is very different for the two superlattice samples. The first sample (produced at 170 °C, spectra a and b) exhibits one fairly well-defined peak, while the sample produced at elevated temperatures (300 °C, spectra c and d) clearly exhibits a broad structure in this spectral region, which is associated with (at least) two peaks. Based on the information derived from the reference samples in Fig. 1, we identify the intensity at lower emission energy (151.1 eV) with Cd 4d states, while the intensity at higher emission energy (151.6 eV) stems from Zn 3d states, as marked in Fig. 2.

This interpretation is corroborated by a peak fit analysis, which is also shown in Fig. 2 (solid lines). All spectra could be well reproduced by a set of 5 peaks and a cubic background. It should be noted that this spectral region does not just simply contain the density of states associated with localized core levels, but rather the spectral signature of low-lying band states on a non-negligible background. Therefore, a peak fit analysis becomes very complicated and somewhat ambiguous. As can be seen from Fig. 2, however, the data analysis is significantly more simple when the excitation energy is tuned to  $h\nu=158$  eV in order to reduce the spectral contributions from the S  $2p_{1/2}$  states (spectra b and d). In particular in the latter case (d), the spectral feature between 150.5 and 152.0 eV can be satisfactorily described with two peaks, i.e., a Cd 4d and a Zn 3d contribution.

This finding now gives us a sensitive probe to study the local chemical environment of (buried) S atoms in II-VI-semiconductors. As can be expected from the different growth temperatures for the investigated ZnSe/CdS superlattices, we find a significantly increased fraction of S atoms in a "ZnS-environment" for the high-temperature preparation. Based on the peak fit analysis for spectra b) and d), the Zn-to-Cd area ratio increases from 0.22 to 1.19, which is particularly remarkable in view of the fact that the Zn 3d  $\rightarrow$  S 2p transition probability appears to be significantly smaller than that of the Cd 4d  $\rightarrow$  S 2p transition, as mentioned above. In other words, we find substantial intermixing at the buried ZnSe/CdS interfaces, which is also corroborated by Raman scattering results. Furthermore we can monitor the chemical environment of the sulfur anions involved in these intermixing processes. These findings give an example of the utilization of cross transitions for the study of the local chemical bonding of a particular atomic species and demonstrate the importance of XES for the study of buried atoms and interfaces.

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